Indian J. Phys. **52B**, 442-426 (1978)

Letters to the Editors

Thermodynamic functions of the three isomeric fluoroanilines

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(*Received* 7 *February* 1978)

The interpreted fundamental vibrational frequencies of the three isomeric fluoroanilines namely, ortho-, meta- and para-fluoroanilines as given by Shashidhar & Rao (1970), Kohlrausch *et al* (1935, 1947) and Verma (1977) have been utilised to calculate the thermodynamic functions in ideal gaseous state for the three fluoroanilines at one atmospheric pressure under the usual approximation of rigid rotator, harmonic oscillator model, and the results are reported.

The total energy in a system is given by

$$\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec}, \qquad \ldots (1)$$

where the subscript trans stands for translational, rot, for rotational, vib, for vibrational and elec for electronic.

The partition function Q in terms of energy is given by :

$$Q = \Sigma g_i e^{-\epsilon/kT} = Q_{trans} + Q_{rot} + Q_{vib} + Q_{elec}, \qquad \ldots (2)$$

where g_i is the statistical weight, k is the Boltzmann constant and T is the absolute temperature.

Each partition function may be evaluated separately from eq. (2) and thus the corresponding thermodynamic functions are calculated. Each contribution to the thermodynamic functions are then added to get the total value. The electronic contribution is small and ignored because ϵ_{elec} is large compared to kT at ordinary temperatures. For the other remaining partition functions the standard expressions as given by Colthup (1964) have been used and their contributions to thermodynamic functions have been calculated at various temperatures.

Considering the substituent as single mass point and the molecule planar one, the principlal moments of inertia I_x, I_y and I_z have been calculated (the x and y axes are in the plane of the molecule and z axis is perpendicular to the plane) are given in table 1. The structure parameters used for calculation have been taken from Evans (1960), Allen *et al* (1950), Interatomic Distances, Special publication (1958) and International tables for X-ray crystallography, (1962).

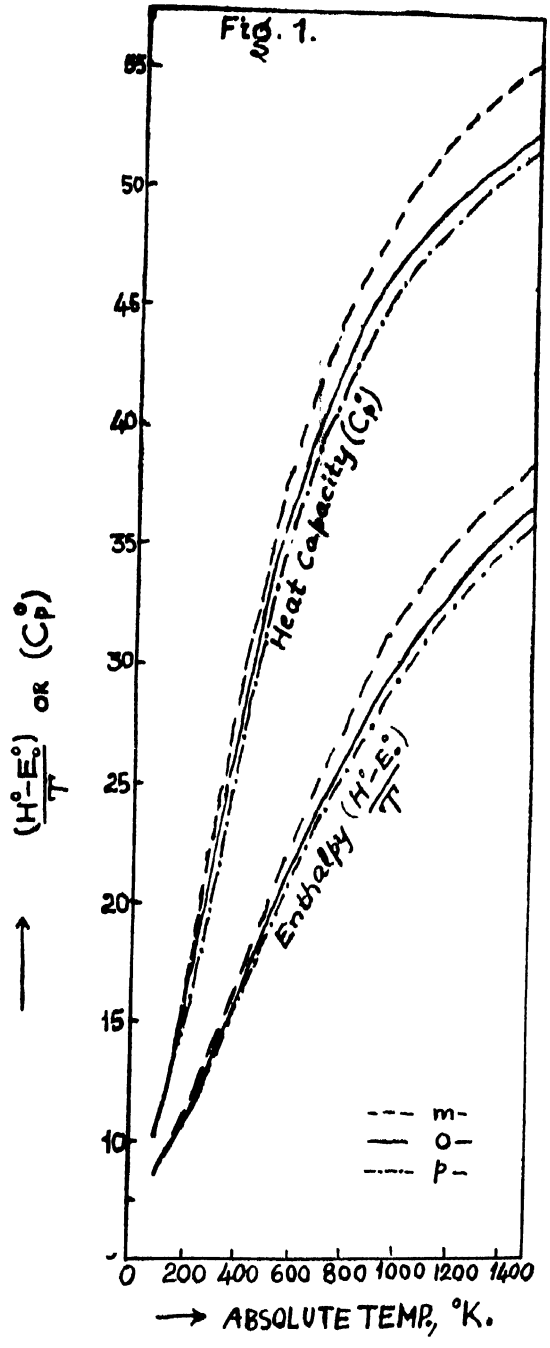

Fig. 1. Variation of enthalpy function and heat capacity with absolute temperatures for ortho-, meta- and para-fluoroanilines.

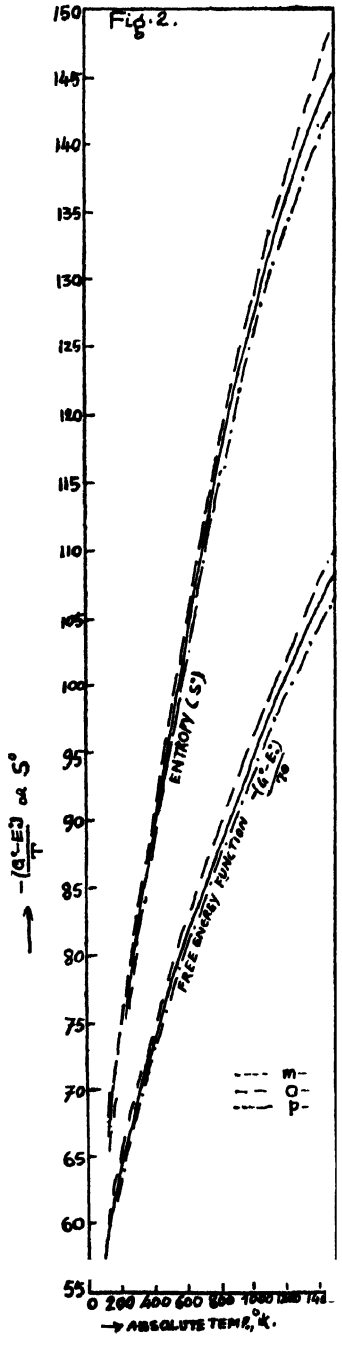

Fig. 2. Variation of free energy function and entropy with absolute temperature for ortho-, meta- and para-fluoroanilines.

Table 2. Thermodynamic functions (in cal-mole/°K) of ortho-, meta- and para- fluoroanilines.

Temp. (°K)	$\frac{(H^0-E_0^0)}{T}$			$-\frac{(G^0-E_0^0)}{T}$			(S^0)			(C_p^0)		
	m-fluoro aniline	*o*-fluoro aniline	*p*-fluoro aniline	*m*-fluoro aniline	*o*-fluoro aniline	*p*-fluoro aniline	*m*-fluoro aniline	*o*-fluoro aniline	*p*-fluoro aniline	*m*-fluoro aniline	*o*-fluoro aniline	*p*-fluoro aniline
100	8·5754	8·5582	8·6697	58·4020	58·4062	57·1822	66·9774	66·9644	65·8519	10·3478	10·2118	10·7402
200	10·8826	10·6788	10·6498	65·0028	64·9503	63·9222	75·8854	75·6291	74·5720	16·1908	15·5095	15·1168
273·16	12·9371	12·3751	12·3338	68·6952	68·5436	67·5505	81·6323	80·9187	79·8843	20·9514	19·9018	19·0650
298·16	13·6798	13·2348	13·1642	69·8593	69·6763	68·6751	83·5391	82·9111	81·8393	22·6048	21·4731	20·8508
400	16·7871	16·1304	15·9064	74·3157	73·9736	72·9161	91·1028	90·1040	88·8225	29·0881	27·6268	26·9730
500	19·8119	18·9700	18·6581	78·3944	77·8756	76·7663	98·2063	96·8356	95·4244	34·5212	32·8404	32·1608
600	22·6489	21·6508	21·2670	82·2275	81·5756	80·4196	104·8764	103·2264	101·6866	38·9177	37·0840	36·3030
800	27·5525	26·3219	25·8417	90·6496	88·4752	87·2252	118·2021	114·7971	113·0669	45·2784	43·1487	42·2860
1000	32·3095	30·1184	29·5947	95·9965	94·7852	93·3762	128·3060	124·9036	122·9709	49·6636	47·2652	46·3617
1500	38·7063	36·8433	36·2103	110·3195	108·3429	106·6479	149·0258	145·1862	142·8582	55·6439	52·6762	52·0555

Under the above assumption ortho- and meta-fluoroanilines belong to C_s symmetry with external symmetry 1 and para-fluoroaniline in to C_{2v} symmetry with symmetry 2, as used by Herzberg (1945).

The total thermodynamic functions, that is, heat capacity (C_p^0) at constant pressure, enthalpy function ($(H^0-E_0^0)/T$), free energy function ($-(G_0-E_0^0)/T$) and entropy (S^0) of these molecules have been given in Table 2; at various temperatures ranging from 100°–1500°K for the ortho-, meta- and para-fluoroanilines and represented by curves in figures 1 and 2. Here E_0^0 is the energy of one mole of an ideal gas at absolute zero, H^0 is its enthalpy and G^0 is its free energy.

Table 1. Moments of inertia in 10^{-40} gmcm^2 for the three isomeric fluoroanilines.

Moment of Inertia (I)	*o*-fluoroaniline	*m*-fluoroaniline	*p*-fluoroaniline
I_x	400·64549	400·64549	564·20084
I_y	309·8021	309·8021	146·2469
I_z	710·448	710·448	710·448

The authors wishes to thank Prof. K. Suryanarayana Rao and Dr. D. K. Deshpande for valuable discussions and suggestions and Mr. P. V. Shanbhag in computational assistance.

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